

COMPLEMENTARY H-BOND PAIRING MECHANISM FOR REPLICATION OF A BINARY POLYPENTOSE SEQUENCE

by

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Summary. Poly(ribulose-1,5-diphosphate) is noted to form a ladder-like structure having two parallel, polyanionic phosphate chains with pentose cross-links. When the phosphate chains are surface-bound, C2 and C3 are elevated above them and C1, C4, and C5 atoms of the pentose. Two distinguishable orientations of the pentose crosslinker then arise: C1→C5 and C5→C1. Hence, polypentose can contain a complex binary sequence. H-bond formation between alcohol and ketone groups at C2 and C3, respectively, of template- and daughter-strand monomers provides a mechanism to obtain the complementary sequence. Since cyclization of ribulose-5-phosphate produces the ribose-5-phosphate in an RNA scaffold, polypentose replication is an apparent antecedent of RNA replication.

Invariance of the 3'-terminal phosphate of glyceraldehyde-phosphate throughout the reductive pentose cycle (RPC) provides evidence of an initial reliance on a polyphosphate scaffold (Davis, 2012). Analysis of genetic code structure and tRNA diversification, deep within the era preceding the Last Common Ancestor (LCA) more than 3.5 billion years ago (Allwood et, 2007; McGuinness, 2010), previously linked an invariant α -carboxylate in intermediates of the ancient pathways of amino acid synthesis, and even more ancient citrate cycle and central trunk pathway from which they branch, to early use of a macromolecular RNA scaffold (Davis, 1999, 2007, 2008, 2009). Production of two glycerate-3-phosphate molecules by cleavage of ribulose-2-carboxy-1,5-diphosphate (triose pair) at its C2-C3 bond, in the RPC, was accordingly considered to represent the conserved trace of poly(triose-phosphate) replication (Davis, 2012). It is noteworthy that formose cycle components glyceraldehyde and its isomer, dihydroxyacetone, both occur as phosphorylated components of the RPC (Davis, 2007). Initiation of the RPC, and accompanying poly(triose-phosphate) replication, thus appears to have been driven by the foregoing components of the spontaneous autocatalytic formose cycle (Butlerow, 1861) reacting with inorganic polyphosphate molecules, bound to a positively charged mineral surface plausibly located at an alkaline hydrothermal vent (Brown and Kornberg, 2004; Achbergova and Nahalka, 2011). Autocatalysis is linked in this scenario with the coevolution of metabolism and macromolecular replication, in accord with earlier inferences on the origin of life (Hinselwood, 1946; Orgel, 2008).

The replicative-form of poly(triose-phosphate) was noted to have polyphosphate chains 8.2 Å apart, cross-linked by ribulose-2-carboxylate molecules (triose pairs) at a spacing

of 2.9 Å (Davis, 2012). Ribulose-2-carboxylate asymmetry implies the polyphosphate chains can be cross-linked in two pentose orientations: $C1 \rightarrow C5$, or $C5 \rightarrow C1$. It follows that the replicative-form of poly(triose-phosphate) could have a complex binary sequence. Since the $C1 \rightarrow C5$ and $C5 \rightarrow C1$ orientations of ribulose-2-carboxylate are distinguishable, they could, in principle, be recognized and cleaved independently. Cleaving and then cross-linking one set of triose molecules to a neighboring polyphosphate chain could, in principle, produce a poly(triose-phosphate) sheet with a distinct distribution of triose cross-links.. Since cleavage of ribulose-2-carboxylate at its C2-C3 bond, in either a $C1 \rightarrow C5$ or $C5 \rightarrow C1$ orientation, produces a pair of glycerate molecules, all sequence complexity is lost during poly(triose-phosphate) replication. Given that complexity transfer is a central feature of polynucleotide replication (Davis, 1979), it may be asked whether this feature arose de novo with quaternary nucleotide sequences, or whether, as seems likely, replication of a simpler sequence preceded it.

Distinct monomer pairs in the replicative-form of poly(ribulose-1,5-diphosphate) are depicted in Fig. 1. Each pentose pair can be seen to contain a specific set of H-bonds. They form between the alcohol and ketone groups at C2 and C3, respectively, between paired pentose monomers of template and daughter strand monomers. In this respect, polypentose resembles a simplified polynucleotide. Rather than a four-letter alphabet though, the sugar sequence is limited to a two-letter alphabet. Unlike polynucleotide replication, however, polypentose replication retains a dependence on attachment to a mineral surface. Attachment to the surface, accounts for the pentose functional groups at C2 and C3 being elevated. This feature of polypentose replication conforms

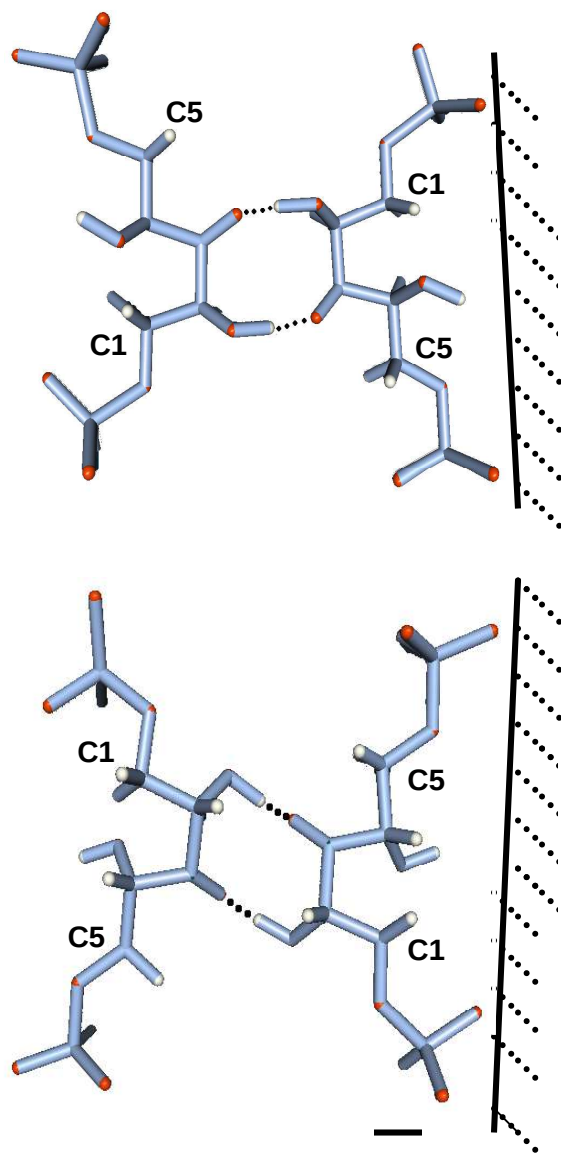


Figure 1. Showing H-bonds between alcohol and ketone groups at C2 and C3, respectively, in paired ribulose-1,5-diphosphate molecules. Pentoses in each pair have opposite orientations: C1 → C5/C5 → C1. At C1 and C5 is a phosphate. Each is in a polyphosphate chain, cross-linked by the sugar, to form a ladder-like structure. The template polymer-ladder is shown attached to a mineral surface (at right). Red denotes an O atom; white an H atom. Bar length is 1 Å. Bond lengths and angles were obtained from Levitt (1983) and Pauling (1960). These pentose pairs were constructed using Facio 16.4.2 model building software (Suenaga, 2008).

with polypentose replication being more archaic than the mechanism of polynucleotide replication.

What the polypentose binary sequences coded for is an open question. They presumably would have needed to code for earlier forms of the molecules encoded by RNA, before the appearance of proteins and their genes. Structural molecules and pre-ribozyme catalysts, almost certainly including metallo-polypentoses, therefore seem likely candidates. Phospholipids account for most of the non-protein constituents of cell membranes, and since they are essentially (triose-phosphate)-fatty acid complexes, modified triose-phosphate sheets, with specified cross-linking patterns, plausibly encapsulated proto-cells of the Poly(pentose-phosphate) Era. Also of interest would be knowing the extent to which proto-cells of this era could generate high energy phosphate from surrounding proton gradients.

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